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Effect of quality of electrolyte fluid on removing MTBE from a clay soil using electrokinetic technique

Abstract

Methyl Tertiary-Butyl Ether (MTBE) is a chemical product and the most commonly used gasoline oxygenate. It is characterized as a pollutant for soil and water that has effects on the human health. Research on the remediation of soil polluted with MTBE is relatively rare. In this paper the results of laboratory experiments to study the feasibility of using the electrokinetic technique to remove MTBE from a clay soil are presented. Tests were conducted on a clay soil contaminated with MTBE in a special apparatus, using different quality of electrolyte and D.C. (Direct Current) or A.C. (Alternative Current) electrical currents. The results of the tests reveal that, under laboratory conditions, MTBE can be removed from the soil by using the electrokinetic technique. The efficiency of remediation is dependent on the quality of electrolyte and type of applied electrical current.

Key words: Electrokinetic technique, MTBE, Electrolyte, Remediation

Introduction

MTBE (Methyl Tertiary-Butyl Ether) originally was used in the 1970s as an antiknock agent for gasoline. It is an oxygen source to improve gasoline combustion and hence reduce pollution from car exhausts (Deeb et al., 2003). MTBE is highly soluble in water and can penetrate to the soil and transfer to groundwater from gasoline leaking from underground storage tanks, pipelines and other components of gasoline distribution system (An et al., 2002). The U.S. Environmental Protection Agency has classified the MTBE as a possible human carcinogen (Johnson et al., 2000). The use of MTBE has been forbidden in the United States since 2003 (Atienza et al., 2005). To date MTBE related problems have spread worldwide including USA, Europe and Asia (Hsieh et al., 2006 and Ayotte et al., 2008). Therefore, there has been a growing concern regarding the treatment of MTBE-contaminated groundwater in recent years (Chen et al, 2008 and 2009).

There are many methods such as bioremediation, temperature treatment, soil washing, solvent extraction and etc. for removal of contaminants from the soil. Electrokinetic is one of the most promising remediation techniques and offers high efficiency and time-effectiveness in remediation of low permeability soils contaminated with heavy metals or organic compounds (Acar and Alshawabkeh; 1993 and Acar et al.; 1995). Electrokinetic remediation is a technique that can be used to treat and remove contaminants from low permeability contaminated soils like kaolinite contaminated with heavy metals and/ or polar organic materials. (Li and Li, 2000). The electrokinetic remediation involves the application of a direct current (D.C.) between electrodes. The application of an electric field to the soil mobilizes charged ions and water to transport pollutants through the soil

towards electrodes by three main mechanisms. These mechanisms are electro-migration, electro osmosis and electrophoresis. Electro-migration explains the movement of ionic species in pore fluid toward oppositely charged electrodes (Altaee et al., 2008). Electro osmosis is defined as the movement of pore fluid. Electrophoresis is described as the movement of charged particles under an electric gradient (Ravera et al., 2006). Previous research has shown that electrokinetic remediation has the potential to remove heavy metals from low permeability soils (Reddy et al., 2003; Reddy and Chinthamreddy, 2003; Zhou et al., 2004 and Wang et al., 2006). Bruell et al. (1992), Acar et al. (1992), Probstien and Hicks (1993), Ho et al. (1999a and 1999b) and Kim et al. (2000), Asadi et al. (2009), Ribeiro et al. (2011), Méndez et al. (2012), and Guedes et al. (2014) showed that the electrokinetic method can be used for removing organic contaminants from the soil.

One of the methods for improving contaminant (metals or organic matters) removal from the soil by using electrokinetic technique is adding a chemical conditioning agent at the anode and/or cathode electrode. The selection of the enhancing agent is dependent on the type of contaminant and soil. Reed et al. (1995), Yeung et al. (1996) and Wong et al. (1997) added EDTA (Ethylene Diaminetetra Acetic Acid) to the cathode compartment for increasing the removal of metals from the contaminated soil. Denisov et al. (1996) added nitric acid to the cathode compartment to increase the removal of Pb from contaminated soil. Shapiro and Probstien (1993) used an alkaline purge solution to increase the rate of electro-osmotic flow and removal of phenol from contaminated soil. Lancolet et al. (1990), Acar et al. (1993), and Kim and Lee (1999) used surfactants for removal of petroleum hydrocarbons, hexa chorohutadien and diesel oil from the soil. Saichek and

Reddy (2005) used a surfactant for enhancing electrokinetic remediation of two kinds of soil contaminated with phenanthrene and found that the surfactant was sufficient for removal of the contaminant from the soil. Han et al. (2009) used EDTA for remediation of a contaminated soil with diesel oil. Kim et al. (2009) used H_2SO_4 and HCl in anode compartment as purging agent. They found that the remediation of soil is improved and the degree of remediation is dependent on the concentration of these agents.

Murillo-Rivera et al. (2009) used NaOH and H_2SO_4 as anolyte and catholyte compositions for removing TPHs (Total Petroleum Hydrocarbons) from low permeability soil by electrokinetic method. They observed the desorption of TPHs from the soil and their transport from the anode to the cathode of the apparatus. A review of the literature shows that research on the remediation of soils contaminated with MTBE is relatively rare. This may be due to the low sorption of MTBE by soil (Yu and Gu, 2006). It has been revealed that existence of MTBE in soil and water has serious effects on the human health because of its carcinogenic behavior. Therefore, remediation of soil and water from MTBE is very important for the human life. Many attempts have been devoted for cleaning polluted water from MTBE by using different methods but the study on remediation of soil is relatively rare. This work presents experimental results on the feasibility of using the electrokinetic technique to transport MTBE through a clay soil. For the first time a number of experimental tests were designed and conducted on a clay soil contaminated with MTBE under constant electric gradient and time with different purge solutions. In addition, two tests were conducted under alternative current (A.C). The results are used to investigate the effect of different quality of electrolyte and electrical current on the efficiency of remediation of contaminated. In what follows the

results are analyzed and compared with each other and the other researchers' results from the literature.

Material

Soil

A kaolin soil was used in this work. The physical and chemical properties and composition of the soil are summarized in Tables 1 and 2. According to the Unified Soil Classification System (USCS) the soil was a clay with low plasticity (CL). Based on the results of standard compaction tests the values of maximum dry unit weight and optimum water content were 17.75 kN/m³ and 17.5% respectively.

MTBE

MTBE was used as contaminant matter. It was a production of Merck Company. It had a molecular weight of 88.15 g/mol, density of 0.7407 g/mL, melting point of -109⁰C and boiling point of 55.2⁰C. Its dielectric constant and sorption coefficient were 2.16 and 1.15 respectively. The values of its diffusion coefficients in air and water were 7.92 (mm²/s) and 9.41e-03 (mm²/s) and its water solubility was 51.26 g/L at 25⁰C.

NaOH and Na₂ SO₄

The experimental values of the electroosmotic mobilities depend on the type of electrolyte and its chemical behavior. In general, in acidic electrolytes at pH less than 2 the electroosmotic velocity is very low but it is strongly increased at pH higher than 4. In order to obtain a reproducible electroosmotic flow, another solution such as NaOH or Na₂SO₄ with concentration of 0.5-1.0 mol/L can be used (Lukacs and Jorgenson (1985).

NaOH and Na₂SO₄ with concentration of 0.1 mol/L were used. They were obtained from a local supplier. NaOH and Na₂SO₄ have been used as purge solution by researchers such as Saichek and Reddy (2005), Kim et al. (2009) and Murillo-Rivera et al. (2009).

EDTA

EDTA is usually used for remediation of soils contaminated with heavy metals. Reddy et al. (2004) examined the effect of EDTA for remediation of soil samples that were contaminated with three different heavy metals. They found it is possible to remove 62-100% of contamination by using 0.1M or 0.2M of EDTA. On the other hand, Yang et al. (2001) and Subramaniam et al. (2004) reported that the chelating agents also desorb Hydrophobic Organic Contaminants (HOCs) by changing the phase properties of the soil organic material. Therefore, it is expected that EDTA would act as a HOC desorbent when it is added as an electrolyte. Han et al. (2009) showed that the use of EDTA results in greater transport and removal of HOCs and removal efficiency increases with increasing the EDTA concentration. Han et al. (2009) used EDTA in their work and concluded that EDTA with concentration of 0.01 M significantly enhances the removal of aromatic hydrocarbon from contaminated soil. In this work EDTA with concentration of 0.2 M was used as Reddy et al. (2004) showed that by increasing the concentration the efficiency of remediation of soils contaminated with heavy metals is increased. Based on the above advantages, it was decided to use EDTA as electrolyte solution for removing MTBE from the soil. Therefore, EDTA was chosen as another purge solution that was used in this work with concentration of 0.2 mol/L. It is a member of the aminopolycarboxylic acid family of ligands. Its density is 292.24 g/mol and its molecular

formula is $C_{10}H_{16}N_2O_8$. Today EDTA is mainly synthesized from ethylenediamine, formaldehyde and sodium cyanide.

Tween 80

The main factors that should be considered in selecting surfactant include biodegradability, low toxicity, solubility at ground water temperature, low adsorption to soil and effectiveness at concentrations lower than 3% (Kimball, 1992). Anionic and nonionic surfactants are less likely to be absorbed to the soil (Mulligan et al., 2001). Tween 80 has the above mentioned characteristics and hence was selected in this work. Tween 80 is from non-ionic surfactants with HLB (Hydrophilic-Lipaphitic-Balance) equal to 13.4. It is a yellow color liquid with chemical formula $C_{64}H_{127}O_{26}$. In this work it was used as an electrolyte with concentration of 3 (weight) percent. Anionic surfactants show relatively lower adsorption to the soil due to their negative charge but interfere with electroosmotic flow. Cationic surfactants may be toxic to microorganisms in the soil (Han et al., 2009 and Kim and Weber; 2003), whereas anionic surfactants are more toxic at lower pH conditions (Kim and Weber; 2003).

Non-ionic surfactants are appropriate for the electrokinetic process because their neutral charge does not affect on electroosmotic flow and they are biodegradable (Mohanty et al.; 2013). Therefore, it was decided to use non-ionic surfactant in this work.

Electrokinetic apparatus

The apparatus used in this work was similar to the one that was used by Mohamedelhassan and Shang (2001) and Ritirong et al. (2008) for simulating the contaminant transport. The schematic plan of the apparatus is shown in Fig. 1. This apparatus consists of a main cell with length and height of 100 and 250 mm that was

made of a Plexiglas with 10 mm-thickness. The main cell is also equipped with a loading frame and a direct current (D.C.) power supply. At each sides of the main cell two reservoirs were added that are referred to as the anode and cathode reservoirs. The reservoirs were connected to the main cell through perforated Plexiglas sheets. These reservoirs can be filled by desired fluid and the total hydraulic head in them can be controlled by adjusting two identical standing tubes through valves. In the main cell two electrodes, EVDS (Electrical Vertical Drains), made of copper foil covered with conductive polymer were vertically installed at a distance of 50 mm from the mass of soil. Jeon et al. (2010) and Kim et al. (2009) used filter paper and porous stone between soil and electrode compartments to prevent from loss of soil. In this work, sheets of geotextile were used. Since these sheets were normally unsaturated, before using they were saturated by flooding in the same liquid as the one in the anode and cathode reservoirs and then they were used at the two sides of sample. Therefore, they can not absorb the pore water from the sample and sample remains in saturated condition. The variations of electrical potential along the length of soil sample were measured during the test through a number of voltage probs. They were installed at the bottom of the main cell at distances of 20, 50, 80 and 110 mm from anode. Load was applied to the soil in the main cell through a loading system. The loading system consisted of two plates, one placed on the top of the sample and one at the bottom and the plates were connected to each other through a bar. The bar was covered with a foam material to isolate it against electrical current. The vertical deformation of soil due to settlement was measured by a dial gauge that was placed on top plate of the loading system. The D.C. current was provided from a power supply. It consisted of a generator that was used to produce different ranges of

voltage and was connected to the EVD through a special connection. The applied voltage in this work was 0.2V/mm for duration of 14 days.

Sample preparation

Information about the maximum adsorption of MTBE by soil was needed before conducting the main tests on contaminated soil samples. Therefore, the adsorption capacity of soil for MTBE was determined through adsorption tests. The tests were conducted on soil contaminated with different percents of MTBE at room temperature. The amount of MTBE adsorption by soil was calculated from the difference in the concentrations of MTBE between the original sample and the supernatant at the end of the experiments (Estabragh et al., 2016). Fig.2 shows the results of adsorption tests. As shown in this figure, the maximum adsorption of MTBE was 1.15 g/kg for this soil. Although the maximum adsorption was 1.15 g/kg of soil, but it was decided to use the concentration of 0.5 g/kg soil. This concentration is the highest amount of MTBE that is adsorbed by the soil and its removal would require its desorption into the pore fluid and advection/migration towards the cathode (Estabragh et al., 2016). Acar et al. (1992) reported that the amount adsorbed phenol by kaolin was about 1.1mg/g but they decided to use 0.5 mg of phenol per gram of soil because most of phenol is adsorbed by soil.

For each test, nearly 8 kg of soil was grounded and the selected soil was divided into 8 portions, each with a mass of 1 kg. The amount of 0.5 g MTBE was mixed with 480 g water so, the ratio of MTBE to soil was 0.104% with concentration of 1.04 g MTBE per one liter of water. Each prepared of soil portion was mixed with 480 ml of the prepared contaminated liquid that consisted of water and MTBE. By adding this volume of liquid to the soil it was changed to slurry form. The mixing of soil and liquid was done by hand

for about 30 minutes in order to allow the uniform distribution of MTBE in soil and obtain equilibrium between the liquid phase and soil. The measurement of water content of this mixture showed that it (i.e. 48%) was more than the value of its liquid limit. The sample in the main cell of the apparatus should be saturated. It was decided to saturate the sample before moving it to the main cell. Soil at water content more than liquid limit (LL) is in the slurry condition and saturated. The results showed that LL of the soil was 44.5% but to have a margin of safety a slightly higher water content of 48% was chosen to ensure saturation. Based on this water content the volume of water for saturation of 1 kg soil was calculated as 480 ml. To this volume of water 0.5 g MTBE was added and mixed by shaking. Then it was added to the soil in increments and mixed regularly during addition to the soil. The slurry method was also used by Mohamedelhassan and Shang (2001) for study of the effects of electrode material and current intermittence in electro-osmosis.

The placement of electrodes (anode and cathode) in the apparatus was similar to the method that was used by Han et al. (2009) and Kim et al. (2009). The prepared slurry was carefully transferred to the main cell in several layers. Each layer was shaken to remove air and achieve uniform compaction. When the soil was fully packed into the main cell a saturated geomembrane was placed at the top of the soil and a pressure of 22 kPa was applied on it. Rittirong et al. (2008) showed that increasing the applied voltage for a specific electrolyte and time can result in variations in the values of pH at cathode and anode reservoirs (increase in cathode, decrease in anode) and increase in the cumulative volume of removed fluid from the soil. Saichek and Reddy (2005) used D.C. current with 0.2 V/mm voltage gradient in their work for remediation a soil contaminated with

Polycyclic aromatic hydrocarbon (PAH). Estabragh et al (2016) indicated that for a constant time of test and a specific electrolyte the efficiency of remediation is increased by increasing the gradient of voltage. The existing D.C. supplier can produce the maximum gradient of 0.2 V/mm. Therefore, to achieve a higher efficiency of remediation, 0.2 V/mm was chosen.

After finishing each test a layer with thickness of about 50 mm from top of the main cell was trimmed and moved from the cell. Then a number of samples were extracted from this surface with equal distances for determination of the degree of remediation. The EPA 3550 standard was used for separating the liquid and solid phases from each other. According to this standard, 2 g of extracted soil at saturation state was poured in a beaker with capacity of 20 ml. The volume of this solution was increased to 10 ml by adding a suitable solution in two or three stages while it was mixed during addition of the solution. Then the liquid phase of the resulting solution was separated by using vortex apparatus and centrifuge. The liquid phase was filtered through a 0.45 μm membrane to remove suspended particles. The filtered liquid was then used to determine the amount of MTBE. GC (Gas Chromatography) apparatus was used for analysis of the liquid phase. The model of the GC apparatus used was PU-4410 which was manufactured by Philips Company. The temperatures of injector, detector and its column were 200°C, 220°C and 100°C. The GC apparatus was calibrated using external standards prior to performing the chemical analyses. A standard pure compound was injected to the apparatus and the peak in the chromatogram was assigned based on the retention time of the standard. The peak areas or heights were used to determine the concentration of released contamination from the sample. Comparing the response of the unknown concentration to that of the known

(standard) concentration was used to determine the amount of concentration in the released leaching liquid.

Experimental test methods

The experimental tests in this work were divided into two groups as shown in Table 3. The total numbers of tests were 5 and 3 for the groups 1 and 2 respectively. For test 1 from group 1 the two reservoirs (anode and cathode) were filled of distilled water. For the rest of tests (2, 3, 4 and 5) in group 1 the anode reservoir was filled with different chemical solutions (NaOH, Na₂SO₄, EDTA, Tween 80) and the cathode reservoir in any condition was filled of distilled water. The applied electrical gradient was 0.2V/mm with duration of 14 days (except test1 that had duration of 7 days). The number of tests in the second group was 3. The anode reservoir in this case was filled with a solution of Tween 80+NaOH and the cathode reservoir was filled with distilled water. In this group, for the first test the D.C. current was applied with duration of 14 days. For the second and thirds tests in this group, A.C. currents with alternative times of 3 and 12 hours were applied by using a transformer. The electrolyte fluid of tests 2 and 3 and the duration of the tests were the same as test 1 of this group. However, after placing the soil sample in the main cell, the anode and cathode reservoirs were filled with desired fluid and a surcharge load of 22 kPa was applied on the soil through the lower plate of the loading system. The vertical deformation of sample was measured using a dial gauge and recoded at different time intervals. The vertical deformation was stopped nearly after 5 days. This stage of test program is called preloading stage which is used for compression of the soil before conducting the next stage of test. After the preloading stage, the hydraulic gradient between the anode and cathode reservoirs was set zero by controlling the level of fluid at

the two reservoirs at the same level. The values of pH in the anode and cathode reservoirs, the intensity of electrical current and the volume of fluid that flowed out of the cathode reservoir were measured during each test. At the end of the test the existing fluids in anode and cathode reservoirs were emptied and a total of 5 soil samples were taken from the soil in the main cell. The samples were taken from the middle section of the main cell by removing the upper layer. The obtained samples were in a longitudinal direction with the same distance from the anode reservoir. GC (Gas Chromatography) apparatus was used to determine the concentration MTBE in the samples.

Results

In this work 8 tests were performed on samples contaminated by MTBE with different electrolyte fluids. D.C. electric current was applied for 6 of the samples and for the rest of them A.C. current was used with periodic times of 3 and 12 hours. The obtained results are as follows:

pH

The results of variations of pH for the test group 1 (tests 1, 2, 3, 4 and 5) and test group 2 (tests 1, 2 and 3) are shown in Figs.3a and 3b. The results of pH for test 1 (Fig.3a) of group 1 (distilled water as electrolyte) show that the value of pH is decreased at anode and increased at cathode from its initial value. The values of pH at the end of the test at anode and cathode reservoirs are 1.3 and 10.92 respectively. Comparison of these results with those of other tests (2, 3, 4, and 5) in group 1 shows that at the end of tests there is an increase in the value of pH at both anode and cathode reservoirs (except tests 2 and 3) particularly in test 5. It is resulted from the tests conducted at constant gradient of voltage and duration of time that the type of electrolyte has a significant effect on the changes of

pH. The value of pH at cathode was more than anode for all conducted tests. It can be concluded that for a given gradient of voltage and duration of time, the type of electrolyte is important in the variations of pH. The variations of pH for tests in group 2 (Fig.3b) show that there is a reduction in the value of pH at cathode for tests 2 and 3 in comparison with the results of test 1. The results show that at the same condition of electrolyte, gradient of voltage and duration of test, the type of electric current is also effective in the variation of pH.

Electrical current intensity

Figs.4a and 4b show the variations of electrical current intensity for different electrolytes (group 1) and electric currents (group 2) respectively. As shown in these figures the value of current intensity is dependent on the time; by increasing the time the value of current intensity decreased for both groups. Comparing the results of test 1 with other tests in group 1 shows that the final value of current intensity is dependent on the type of electrolyte fluid. The final value of current intensity for the samples with distilled water as electrolyte is 0.064 amp (A) but for the solutions of NaOH, Na₂SO₄, EDTA, and Tween 80 it is changed to 0.17, 0.14, 0.088 and 0.11 A respectively. It is seen that the final values of current intensity are not the same and are dependent on the electrolyte fluid that is used in the test. In the second group the electrolyte solution was a mixture of Tween 80 and NaOH. The value of current intensity for test 1 is 0.187 A and it is changed to 0.311 and 0.28 A for tests 2 and 3.

Discharge flow

Figs. 5a and 5b show the cumulative discharge from the sample for different tests with different electrolytes (group 1) and different electric currents (group 2). As shown in

Fig.5a, the amount of discharge at the end of test 1 is 333.5 ml and it changes to 506, 624, 549.5 and 749 ml for tests 2, 3, 4 and 5 of group 1 respectively. In the second group the discharge of the sample with Tween 80 and NaOH is 902 ml but it changes to 1026 ml for period of 3 hours and 840 ml for 12 hours.

Electro-osmotic permeability (K_e)

Electro-osmotic permeability (K_e) governs the water flow in a soil mass under an electrical gradient in a similar way as hydraulic conductivity governs the flow in soil under hydraulic gradient. The value of K_e was calculated from cumulative volume of the fluid removed from the soil according to the method that was proposed by Mohamedelhassan and Shang (2001). The variations of K_e for the two groups of tests are shown in Figs.6a and 6b. The value of K_e for distilled water is $0.03 \times 10^{-3} \text{ mm}^2/\text{v}.\text{sec}$ and it changes to 0.996, 0.123, 0.108 and $0.147 \times 10^{-3} \text{ mm}^2/\text{v}.\text{sec}$ for the cases of NaOH, Na_2SO_4 , EDTA and Tween 80 as electrolyte (Fig 6a). In the second group the value of K_e for the mixture of Tween 80 and NaOH is equal to 0.177×10^{-3} and it is changed to 0.170×10^{-3} and $0.165 \times 10^{-3} \text{ mm}^2/\text{v}.\text{sec}$ for the tests with same electrolyte as test 1 of this group but under A.C. current with alternative times of 3 (test 2) and 12 hours (test three). By increasing the alternative time the value of K_e is decreased.

Remediation

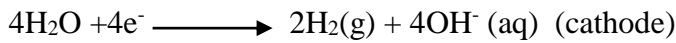
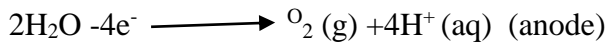
Figs.7a and 7b show the amounts of removal MTBE from the soil samples for tests of groups one and two. The results show that when the electrolyte is distilled water, the percents of removal of MTBE around the anode and cathode are 6.8% and 0.75% respectively. This indicates that a greater percent of removal of MTBE occurs near the anode and by increasing the distance from anode the percent of removal of MTBE is

decreased. This trend of removal of MTBE can also be seen for other tests of group 1 (see Fig.7a). Comparing the results of test 1 with other tests in this group shows that changes in type of electrolyte fluid has effect on the removal of MTBE from the soil. When the solution of SO_4Na_2 is used as electrolyte, the percents of removal of MTBE are 34.4, 32.8, 25.7, 25.2 and 15.0% at distances 50, 100, 150, 200 and 250 mm from the anode towards the cathode respectively. These values of remediation are changed to 41.5, 39.6, 26.3, 24.0 and 21.4 % when Tween 80 is used as the electrolyte fluid. Fig.7b shows the remediation results for the tests in group 2. The results for mixture of Tween 80 and NaOH are 62.4, 61.9, 53.5, 40.4 and 39.0 % at distances of 50, 100, 150, 200 and 250 mm from the anode. In test 2 of this group in which the alternative period is 3 hours, the percents of removal of MTBE at the above locations are changed to 55.9, 52.5, 51, 52 and 53.9 % and for test 3 (12 hours alternative) they are changed to 58.7, 49.7, 47.2, 48 and 57.0%. Comparing with the results of test 1 in this group it is shown that the A.C. current can increase the remediation of soil near the cathode and increasing the alternative time is a effective in removal of MTBE from the soil.

Discussion

The electrokinetic technique can be used for remediation of contaminated clay soil. Negative charges are present on the clay mineral surface due to the isomorphic substitution or broken bonds. These negative charges may be balanced by adsorbed cations and associated anions that are present as salt precipitates and when the particle surface is covered by water, the precipitated salts go into solution (Mitchell; 1993). When they are dissolved in the solution, the cation concentration is decreased by increasing the distance from the clay surface until the concentration becomes the same as the

concentration of ions in solution. However, the negative electrical field originating from the particle surface counteracts the diffusion process and the cations and anions distribute themselves in a diffuse double layer configuration (Mitchell; 1993). The results of the tests (Fig.3) show that, in general, the value of pH is decreased and increased in anode and cathode reservoirs during the tests. When a direct current creates a voltage, due to the difference between the two electrodes, different reactions occur in the soil water system. Hydrogen gas is produced in the cathode and the surrounding pore fluid solution becomes basic with pH in excess of 10 while at the anode oxygen is yielded. These reactions are as follow:

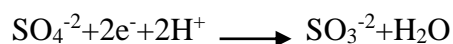


The production of H^+ ions at the anode creates an acid front (Hamed et al., 1991) which moves from anode to cathode by migration, diffusion and convection. As the acid front moves from the anode to cathode the H^+ ions are exchanged with the adsorbed cations in the diffuse ion layer around clay particles. However, at the cathode a base front is developed and the hydroxide ions that are formed at the cathode migrate to anode. The values of pH at anode and cathode (Fig.3) are consistent with the results that were reported by Acar et al. (1989) and Hunter (1981). Hamed et al. (1991) indicated that the decrease in the value of K_e is due to advancing of acid front from the anode to cathode.

The results show that when distilled water is used as electrolyte (Fig.3a) the final values of pH at the anode and cathode reservoirs are 1.3 and 10.92 respectively. Adding solution of NaOH at anode changes the values of pH at anode and cathode reservoirs to 4.21 and 13.09. Increasing the value of pH at anode causes reduction in the number of H^+ ions at

the anode reservoir. Therefore, the clay particles take less positive charge. This results in the zeta potential not being charged by positive charge. According to the Helmholtz-Smoluchowski (H-S) theory the flow to the cathode increases. Consequently, some of OH^- is moved to the cathode in soil under electric fields due to diffusion and electromigration phenomena and causes increase in the value of pH at cathode.

The role of Na_2SO_4 is similar to the NaOH ; it produced SO_4^{2-} and neutralized some of H^+ ions generated at the anode and caused increase of pH from 1.3 for distilled water to 1.71. According to the following reaction, SO_4^{2-} can neutralize the proton H^+ and produce water at anode that leads to increase in pH at anode:



The migration of Na^+ ions toward the cathode increased the intensity of current to 0.14 amp.

The results for the tests with EDTA as electrolyte show that the values of pH at anode and cathode are 1.3 and 13.14 that are slightly higher than the values when distilled water is used as electrolyte. It can be said that EDTA is an alkaline matter and its solution can react with H^+ that is produced at anode. It can neutralize the H^+ and cause increase in pH value at anode. By migration of some of OH^- to the cathode the value of pH is increased in comparison with distilled water. The results show that when the solution of Tween 80 is used, the values of pH at anode and cathode are slightly higher than the corresponding values with distilled water as electrolyte. Although Tween 80 is a nonionic and neutrally charged surfactant but several investigators such as Rosen (1989), Edwards et al. (1994) and Ko et al. (1998) have shown that nonionic surfactants may obtain charges and/or become protonated. This suggests that the adsorption of the surfactant molecule to the

mineral surface reduces the adsorption of mobile ions such as H^+ , Al^{+3} or Ca^{+2} , thereby allowing these ions to produce a higher current as 0.11 mA in comparison with distilled water that is 0.064 mA. Moreover, surfactant molecule adsorption displaces and releases ions that had been previously adsorbed to the surface of particles and causes changes in the pH values of the two reservoirs. When purging solution is the mixture of Tween 80 and NaOH, in this case by considering the above discussion for the mechanism of Tween 80, the NaOH also produces Na^+ and OH^- , so a number of H^+ ions that are produced due to the electric current are neutralized by OH^- . Therefore, both Tween 80 and NaOH are effective in changing the pH and increasing the current intensity. In the case of A.C. current with 3 and 12 hour periods, it is observed that the variation of pH and current intensity is more than the test with the solution of Tween 80 and NaOH with D.C. current. These changes are due to the migration of some of OH^- from the cathode to the anode that are effective in neutralizing the H^+ in anode and causing increase of pH at anode and decrease of pH at cathode. The current intensity is higher in the case of A.C. current than the case of D.C. A system of clay and water (electrolyte) consists of clay particles with negative charge that are surrounded by diffuse double layer (DDL). By applying a D.C. current to the soil, polarization occurs for clay particles and DDL. This charge for the DDL is more than the particles. Therefore a new charge orientation of ions is formed against applied current which reduces the effectiveness of the electric field to move water and hence decreases the amount of transported ions. The A.C. current allows the DDL layer to recover its original charge distribution and it can reverse the polarization process. It can be said that more water flows to the cathode in comparison with D.C. current and more ions are transported.

The results show that for the case of A.C. current, the intensity of current with periodic time of 3 hours is more than that with 12 hours. This could be because for the longer period of time (12 hours) there is enough time for the existing ions in the solution to react with other chemicals in the solution to produce precipitated salt or react with clay particles.

The results in Fig. 5a show that the cumulative volume of fluid outflow from the sample for distilled water is 333.5 ml and it is increased to 549.5, 624 and 749.7 ml when the electrolyte is changed to solutions of EDTA, Na₂SO₄ and Tween 80 respectively. It is resulted that the discharge of fluid flow out of sample is dependent on the quality of the electrolyte fluid. According to the Helmholtz-Smoluchowski (H-S) equation the average electroosmotic flow velocity (v_{eo}) can be obtained by the following relationship (Eykholt and Daniel, 1994):

$$v_{eo} = -\frac{D\varepsilon_0\zeta}{\eta}E_x \quad (1)$$

where E_x , D , ζ , η are electrical gradient, dielectric constant, zeta potential and viscosity respectively. ε_0 is the permittivity of vacuum equal to 8.854×10^{-12} C/Vm. Saichek and Reddy (2004) indicated that Zeta potential is dependent on several factors including the charge on the surface of particles and conductivity of the pore solution. The zero point of charge (ZPC) is referred to the pH value at which the net charge on the surface of particles is zero (Eykholt and Daniel; 1994 and Saichek and Reddy; 2004). When the value of pH is above the ZPC the zeta potential of soil is negative and electroosmotic flow occurs toward the cathode. Conversely, when the pH is less than ZPC the zeta potential is positive and the osmotic flow occurs to the anode. Therefore,

the amount of cumulative water that flows out of the sample is dependent on the zeta potential. So, the decrease in the volume of water is resulted from the increase of zeta potential due to decrease in pH in the soil. Therefore, the value of zeta potential is decreased by increasing pH in the test and it leads to reduction in the value of K_e . Fig.5a shows the results of the first group of tests. As shown in this figure, the final cumulative volumes of fluid from the soil for distilled water, NaOH, EDTA, Na_2SO_4 and Tween 80 are 335, 506, 549.5, 625.3 and 749.7 ml. These data show that the outflow of fluid is dependent on the type of electrolyte because the applied voltage and duration of tests are the same. It is shown that the zeta potential for distilled water is more than the other electrolytes and its value for Tween 80 is the least amongst the used electrolytes. The results of cumulative water outflow from the sample for the second group are shown in Fig.5b. It is seen that the volume of outflow for electrolyte Tween 80+NaOH is 902 ml and for Tween 80 is 749.7 ml. Therefore, zeta potential for the case of Tween 80 as electrolyte is more than Tween 80+NaOH. The results show that volume of outflow of liquid for electrolyte with A.C. current for 3 and 12 hours is nearly equal to 845 ml. It is indicated that the zeta potential for them is less than the same electrolyte but under D.C. current.

It is resulted from the volume of cumulative discharge of fluid from the sample during the tests that the value of zeta potential for the different electrolytes used in this research is more than its value for distilled water which caused greater discharge of fluid out of the sample. It can be said that the amount of zeta potential is dependent on the quality of electrolyte because the different ions that are produced by the used electrolyte may change the charge on the particle surface that could in turn change the pH condition of

ZPC and finally the value of zeta potential. The final volume of discharge of fluid from the sample when the electrolyte was distilled water was 333.5 ml but it was 506 ml for NaOH. NaOH produced Na^+ and OH^- ions that influenced the charge of particle surface of clay and changed the zeta potential which increased the volume of outflow of fluid in comparison with the distilled water. These results are not in agreement with the findings that were reported by Saichek and Reddy (2003) who concluded, from tests on a soil contaminated with phenanthrene, that the volume of discharged fluid when the electrolyte is distilled water is more than the other electrolytes. They attributed this to the constant dielectric and viscosity of the electrolyte. This may be due to the different contaminating matter that was used in this work.

The electroosmotic flow velocity v_{eo} can be expressed by the following relationship:

$$v_{eo} = K_e E_x$$

where K_e is the electroosmotic conductivity. The results show that during the test for each electrolyte, the value of K_e is decreased with increasing the time. This reduces the volume of discharge flow out of the sample, so the cumulative discharge attains a constant value with passing time. It is concluded that the value of K_e is dependent on the quality of electrolyte. The final values of K_e for distilled water and Tween 80 are 0.03 and $0.148 \text{ mm}^2 \cdot 10^{-3} / \text{v} \cdot \text{sec}$ respectively. This causes the final volume of discharge fluid out of the sample with Tween 80 as electrolyte to be more than the sample with distilled water as electrolyte. As it was explained by the H-S equation, changes in the charge of surfaces of soil particles and pore fluid behavior can influence the discharge of flow out of the sample. Moreover, the electrical gradient may not be uniform throughout the soil which could lead to non-uniform flow of fluid in the sample (Eykholt and Daniel, 1994).

Therefore, the average value of K_e through the soil is generally changed with time and the flow of fluid may be stopped or change in direction.

Fig.7 shows a comparison of removal percent of MTBE from anode to cathode for different electrolytes. Yong (2010) indicated that the mechanisms for binding organic compounds can be through London-Van der Waals forces, hydrophobic reaction, hydrogen bonding, charge transfer, ligand and ion exchange. MTBE is hydrolysis in water which produces an alcohol that can be bind particles of soil by the above mechanism. However, changes in properties such as pH, ion concentration or pore water mineral surface charge affect the removal of MTBE from soil by destruction of the bond between MTBE and soil particles. Distilled water has less effect than the other electrolytes on producing MTBE solution and its migration toward the cathode reservoir. The reduction in the efficiency of remediation can be due to the accumulation of gas at the electrode-soil interface which causes increase in the electrical resistance of the system. However, the accumulation of gas around the EVD electrode causes reduction and inhabitation of fluid flow of the soil that leads to the reduction in the efficiency of remediation by this method. Tween 80 is more effective than the other electrolytes in group 1. In these tests with different electrolytes it is seen that the percent removal of MTBE is high near anode and low near cathode. This indicates that the high flow near the anode has solubilized MTBE allowing it to migrate toward the middle and cathode sections but then there was contaminant deposition or inadequate electroosmotic flow to mobilize the contaminant completely out of the soil or into cathode reservoir. However, the greater flow out of the sample (higher value of K_e) causes a higher percent of removal of MTBE from the soil. Therefore increasing the pH in anode increases the

removal of the MTBE from the soil. Shapiro and Probst (1993) and Schultz (1997) have shown that adding a pH control solution to the anode reservoir helps to neutralize the electrolysis reaction at the anode and the result is a higher and more sustained electroosmotic flow and greater contaminant removal. The results of the tests in group 2 show that the Mixture of Tween 80 and NaOH is more effective in remediation of soil contaminated with MTBE than the other electrolytes that were used in the tests of the first group, but the amount of removal of MTBE is higher near the anode and lower near the cathode.

The results of tests with the mixture of Tween 80 and NaOH as electrolyte under A.C. current for both time periods (3 and 12 hours) show that the percent of removal of MTBE near the anode and the cathode is more than the middle section. For the tests with period of 12 hours the percent of remediation near anode and cathode is slightly more than the test with period of 3 hours. It can be said that advancing of the acid front is effective in removing MTBE. Alshawabkeh and Brika (2000) indicated that since hydrogen ions are smaller than hydroxyl ions and have 1.76 times the ion mobility of hydroxyl ions therefore the acidic front moves faster through the soil.

Air, water and soil form the basic framework for life of the mankind. Pollution of each of these elements can affect the healthy life of the mankind. In this work the remediation of soil contaminated with MTBE was studied through experimental tests by using electrokinetic technique. Based on the obtained results it was shown that the remediation of contaminated soil by MTBE can be achieved by using this method with a suitable purge solution.

Cost-effective remediation of a contaminated soil by electrokinetic technique in the field scale is dependent on engineering factors such as soil characteristics (soil type, void ratio, degree of saturation), site geology, lateral extent of contamination, depth of contamination, topography, location, climate, land usage, and surface and groundwater conditions (Meegoda and Ratnaweera; 1995). The results obtained from laboratory tests and geotechnical site investigation are a base and guide for designing the electrokinetic operation system for the field. Lo et al. (1991) suggested that the depth of electrode insertion should be equal to the thickness of soil layer to be remediated. The upper portion of the electrode in contact with ground surface should be electrically insulated to avoid short circuiting due to presence of surface water (Lo et al.,1991). The material, layout and spacing of electrodes and applied voltage are important factors in designing acceptable field applications. Typical spacing between anode and cathode was recommended to be between 1 to 3 m (Lo et al., 1991). In general, for an approximately uniform electric field, the spacing between electrodes of the same polarity should be much less than spacing of the opposite polarity. The electrical conductivity of the in situ soil and the layout of electrodes influence the required power supply capacity. The balance between the cost and installation of electrodes and efficiency of treatment is important in the final design of the site. Cost can be dominated by external requirements such as the cost of transport or disposal. Some details of design and methods for calculating remediation cost have been published by Alshawabkeh et al. (1999a and 1999b), Ho et al. (1999b) and U.S. E.P.A. (1997).

Conclusion

An experimental program was designed and conducted to study the remediation of a clay soil contaminated with MTBE. The experimental tests were performed in two groups with the same duration of time and gradient of applied voltage. In the first group five different electrolytes were used but in the second group both A.C. and D.C. currents were applied. The following conclusions can be drawn from this work:

- The cumulative discharge of fluid from the sample, current intensity and K_e are dependent on the type of electrolyte.
- Under D.C. current, and given gradient of voltage and duration of time of test, the effect of Tween 80 is more than the other electrolytes in removing the MTBE from the soil. In addition, comparing the results of remediation showed that the mixture of Tween 80 and NaOH (test 1 from group 2) is more effective than the solution of Tween 80 in removing MTBE from the soil.
- For the same electrolyte, gradient of voltage and time of the test, A.C. current is more effective than D.C. current in remediation of soil contaminated with MTBE.

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Table 1. Physical and mechanical properties of soil

Soil properties	Values
Specific gravity	2.71
<i>Consistency limit</i>	
Liquid limit	44.5 %
Plastic limit	15.4 %
Plastic index	29.1 %
USCS Classification	CL
<i>Compaction study</i>	
Optimum water content	17.5 %
Maximum dry density	17.75 KN/m ³
<i>Grain size analysis</i>	
Sand	0.0%
Silt	25 %
Clay	75 %

Table 2. Chemical composition of soil

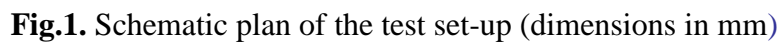
Chemical composition	Quantity (%)
<i>Chemical composition of soil</i>	
Kaolinite	64
Quartz	27
Calcite	2.5
Others	6.5
<i>Chemical composition of clay minerals</i>	
SiO ₂	65
Al ₂ O ₃	25
Fe ₂ O ₃	0.60
TiO ₂	0.05
CaO	1.5
MgO	0.55
Na ₂ O	0.45
K ₂ O	0.36
Others	6.40

Table 3. Characteristics of different tests

Group 1				
Test No.	Fluid of cathode	Fluid of anode	Electricity current	Duration of test (day)
1	Distilled water	Distilled water	D.C.	7
2	Distilled water	NaOH solution	D.C.	14
3	Distilled water	SO ₄ Na ₂ solution	D.C.	14
4	Distilled water	EDTA solution	D.C.	14
5	Distilled water	Tween 80 solution	D.C.	14
Group 2				
1	Distilled water	Tween 80+ NaOH solution	D.C.	14
2	Distilled water	Tween 80+ NaOH solution	A.C. ^a	14
3	Distilled water	Tween 80+ NaOH solution	A.C. ^b	14

a- periodic current = 3 hours

b- periodic current = 12 hours



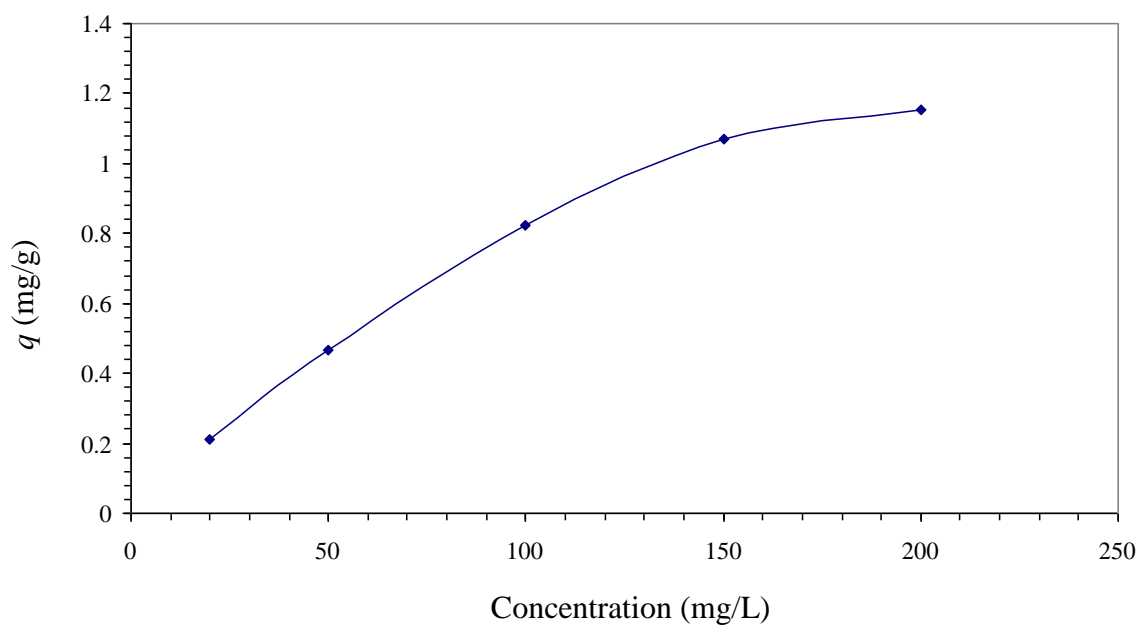
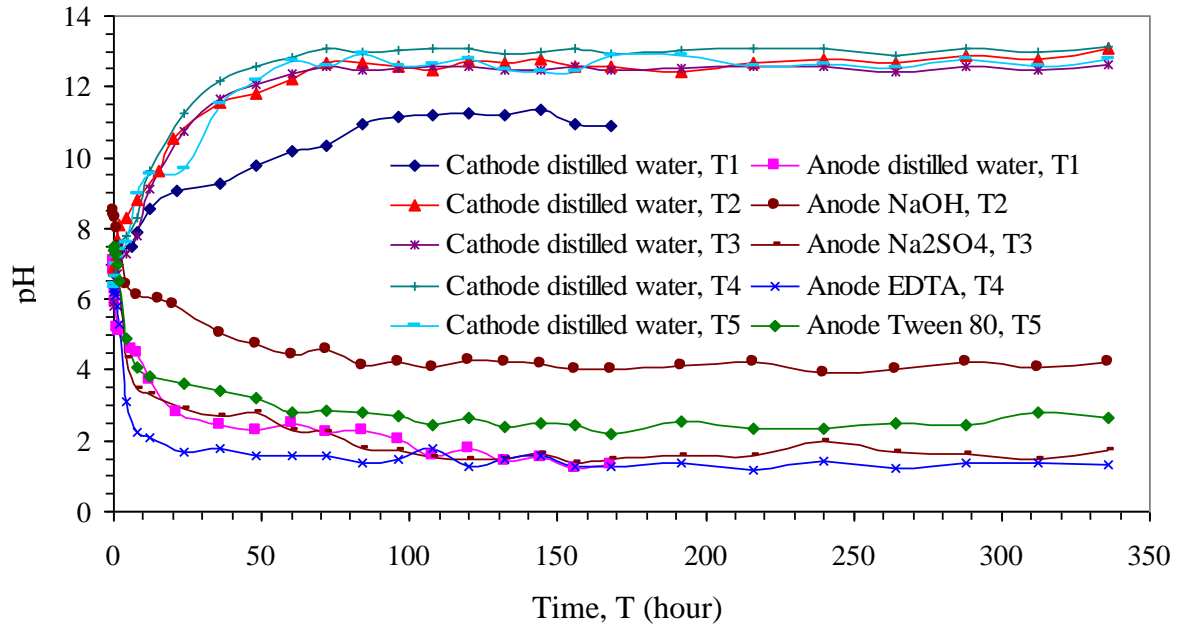
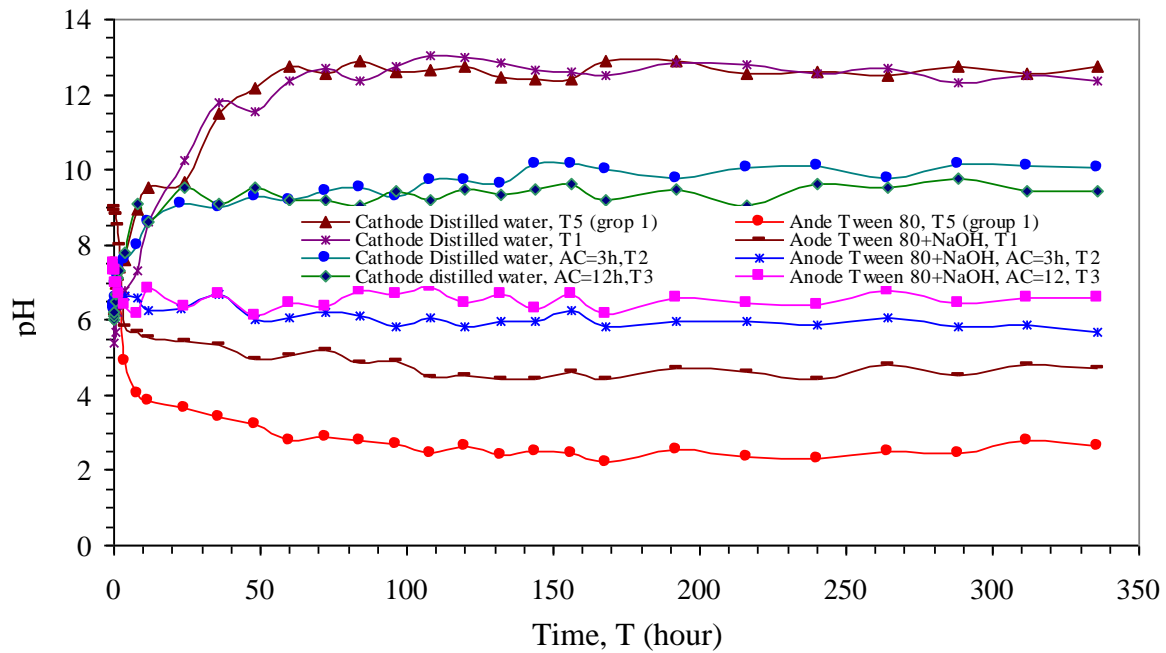


Fig.2. Variations of adsorbed MTBE (mg) per mass of soil (g) with initial concentration of MTBE (mg/L) for contact time of 12 hours



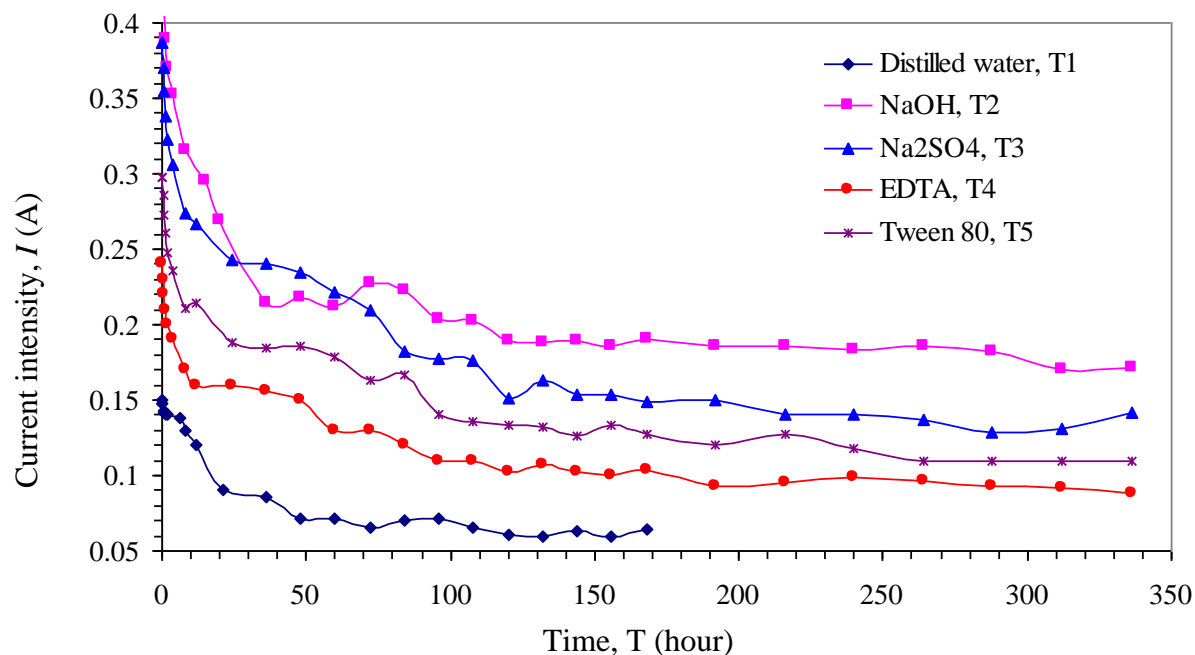
(a)



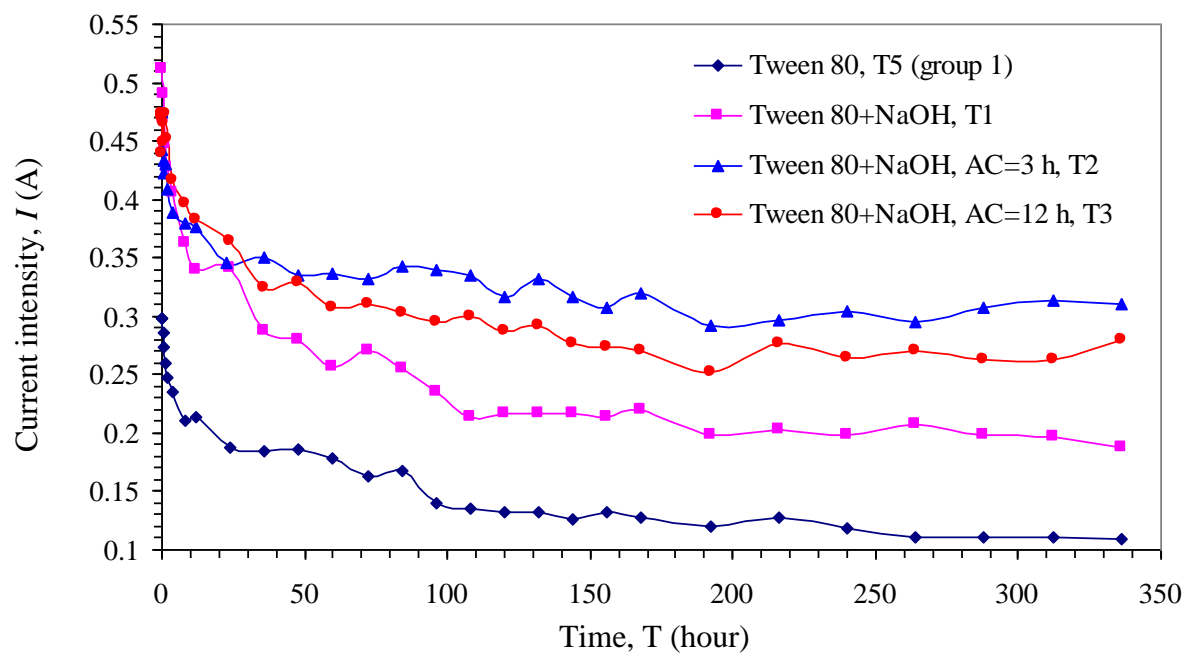
(b)

T= Test

Fig.3. Variations of pH for tests in (a) group 1 (b) group 2 during the tests



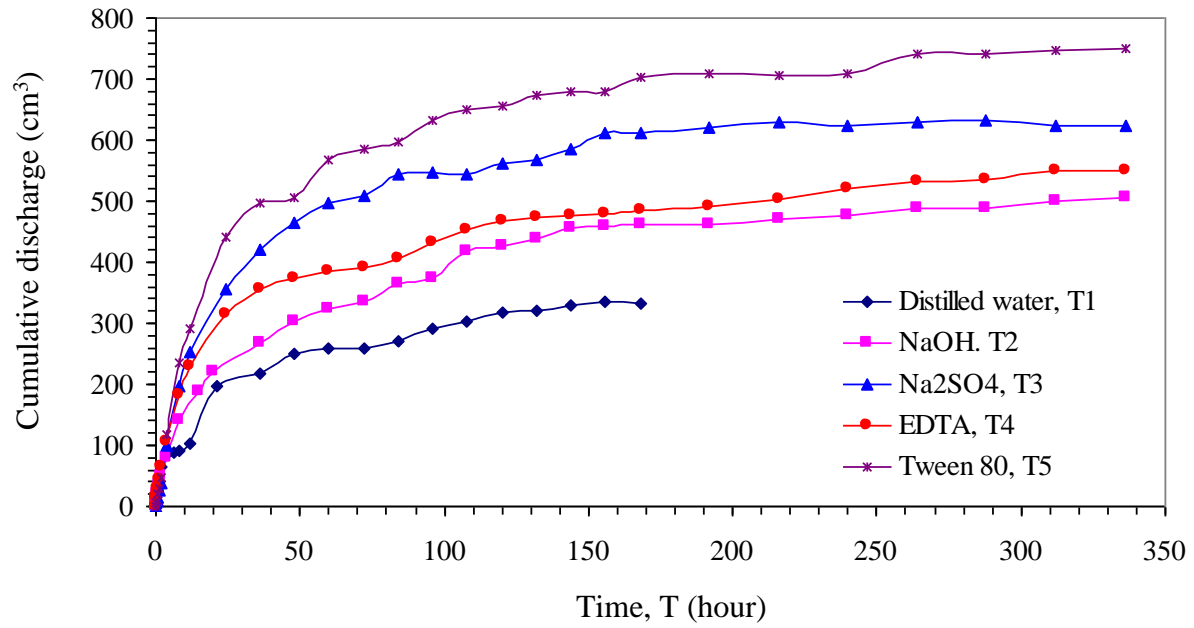
(a)



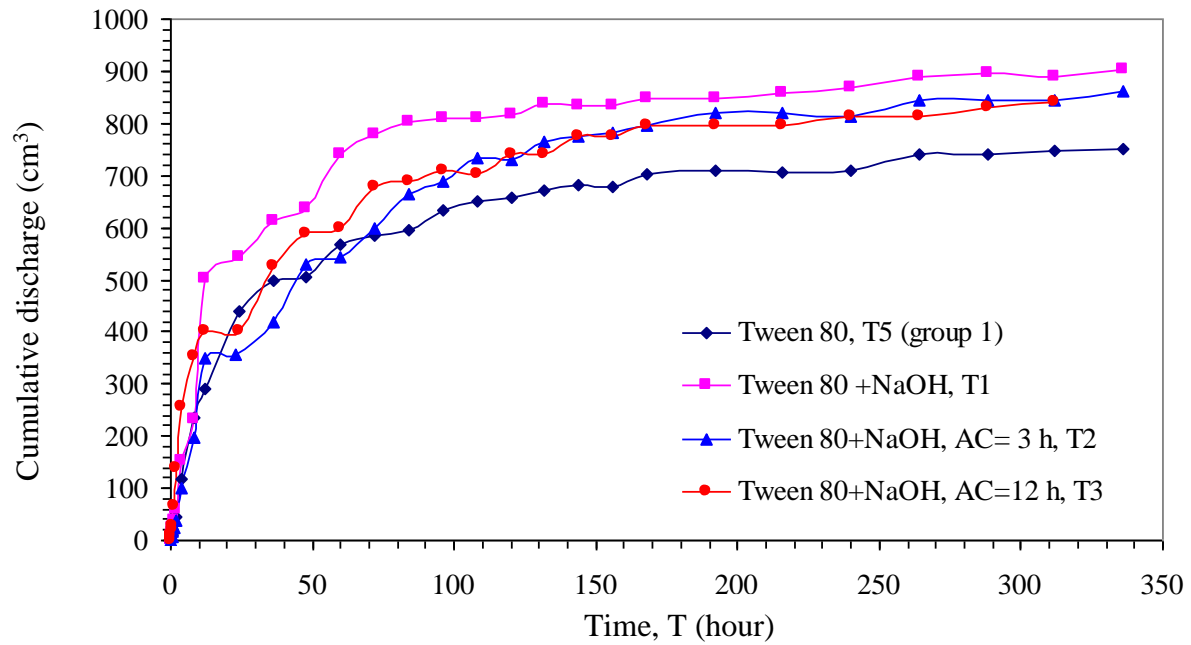
(b)

T= Test

Fig. 4. Variations of current intensity for tests in (a) group 1 (b) group 2 during the tests



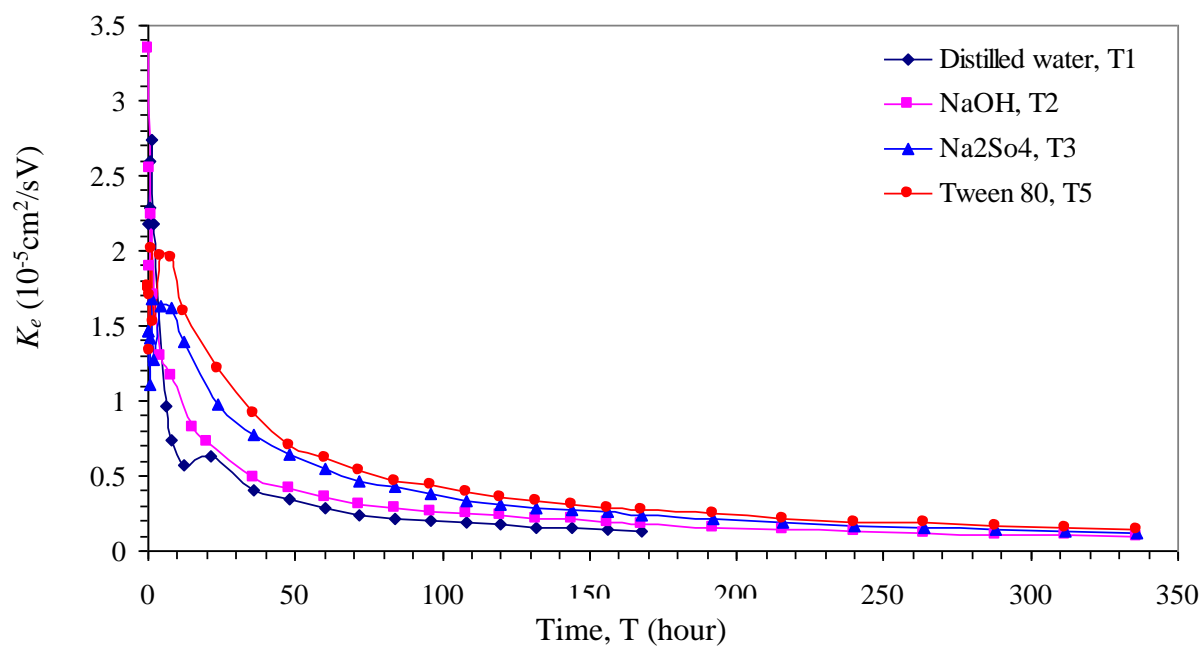
(a)



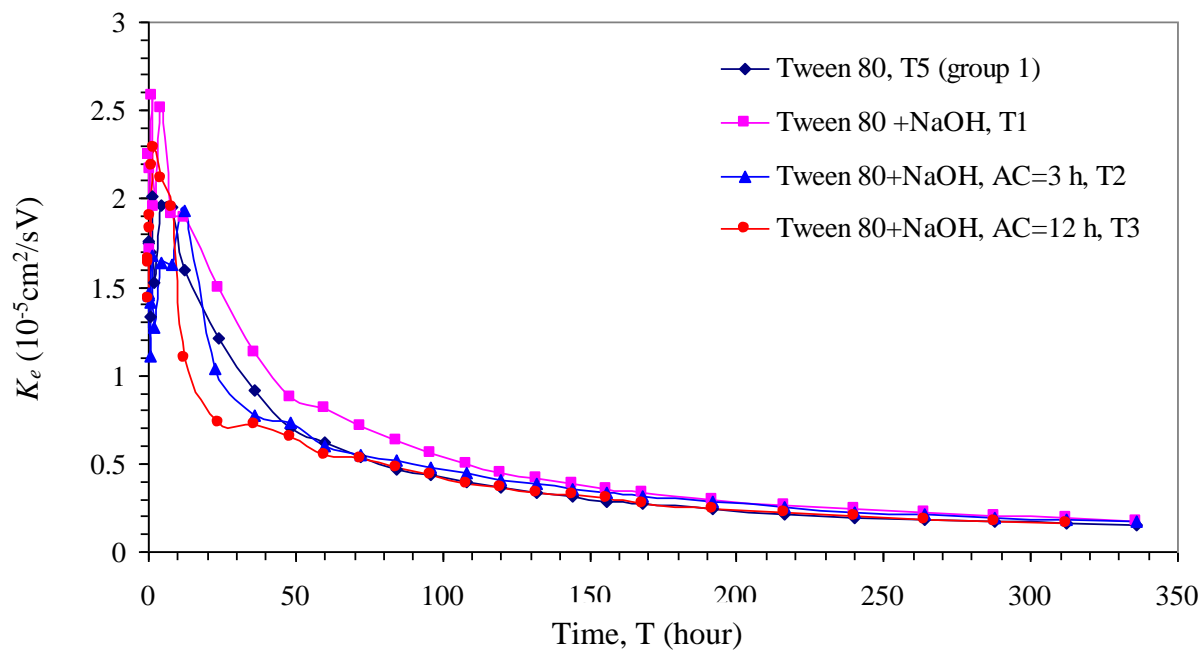
(b)

T=Test

Fig.5. Variations of cumulative fluid flow out of samples for tests in (a) group 1 (b) group 2 during the tests



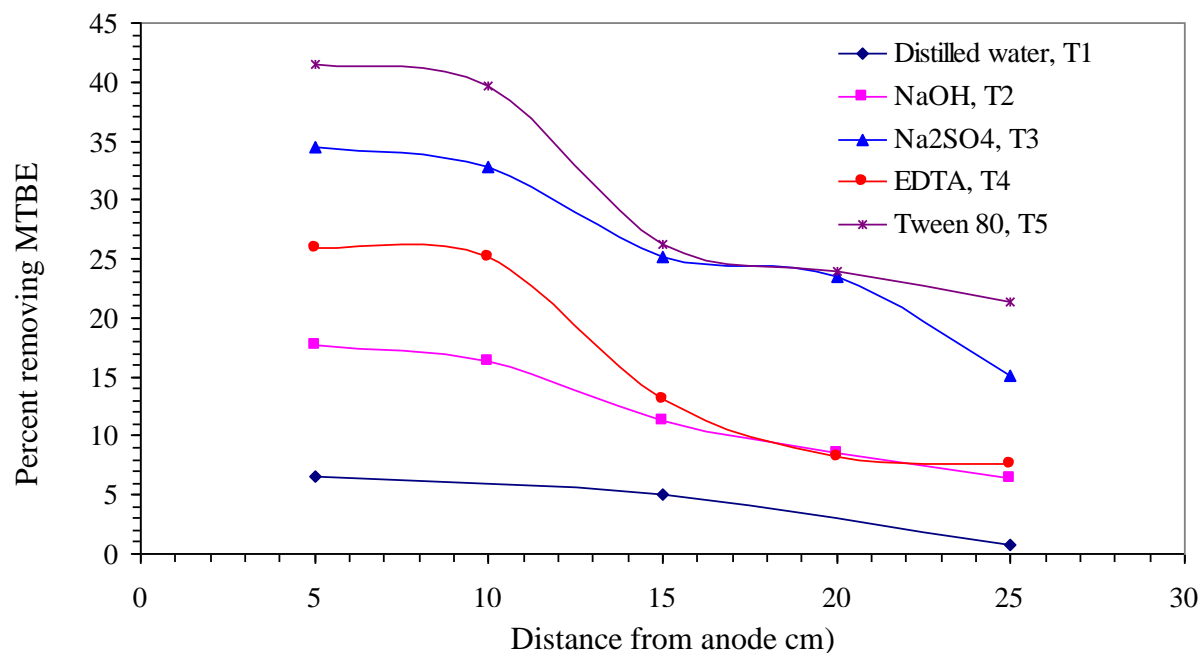
(a)



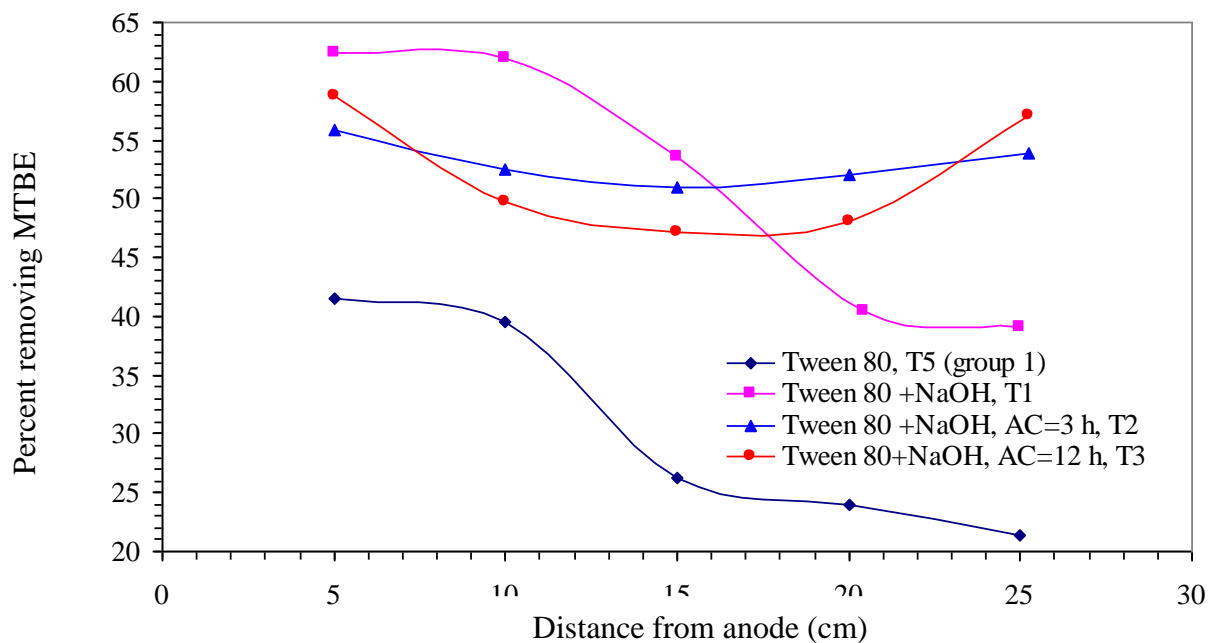
(b)

T=Test

Fig.6. Variations of K_e for tests in (a) group 1 (b) group 2 during the tests



(a)



(b)

T=Test

Fig.7. Percent removal of MTBE from various points of soil sample for tests (a) group 1
(b) group 2